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A slip-link model with 3D network structure

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本研究では，からみあった高分子系の実空間での多体ダイナミクスを高分子鎖の自由エネルギー (J. D. Schieber, J.Rheol., 2003) から記述する．スリップリンク描像に基づき，高分子鎖はからみあい点間分子量程度のチューブセグメントで粗視化する．高分子の運動はチューブセグメント間の化学ポテンシャル差によるからみあい点（スリップリンク）を介した一次元の Kuhn 統計セグメントの輸送運動と，からみあい点の力学的バランスに基づく運動によって表される．本稿では，からみあい点間分子数の確率分布から，本モデルの妥当性を検証した．

In this study, a multi-body slip-link model in 3D space described by total free energy of system is proposed. Though a 3D slip-link simulation based on Brownian dynamics [1] has presented good agreements with rheological properties of various systems, thermodynamical expression has been incomplete. As a promising approach, Schiebers' description [2, 3] based on chain free energy is modified for multi-body motion in 3D space.

A chain is composed of Z strands and each strand has N_i Kuhn steps with length of b. End-to-end vector of the strand is $\mathbf{Q}_i$ which connects consecutive slip-links as $\mathbf{Q}_i \equiv \mathbf{R}_i - \mathbf{R}_{i-1}$. The free energy of a chain is expressed as

$$F = \sum_{i=2}^{Z-1} F_{\mathrm{S}}\left(\mathbf{Q}_i, N_i\right) + F_{\mathrm{E}}\left(N_1\right) + F_{\mathrm{E}}\left(N_Z\right), \tag{1}$$

where F_{S} and F_{E} are free energies of an entangled strand [2]. Kuhn steps transfer through the slip-link by chemical potential differences and Brownian force obeying

$$N_i(t+\Delta t) \cong N_i(t) + \frac{\Delta t}{k_{\mathrm{B}} T \tau_K}\left\{\mu_{i-1}(t) - 2\mu_i(t) + \mu_{i+1}(t)\right\} + \sqrt{\frac{2}{\tau_K}}\left(\Delta W_i - \Delta W_{i-1}\right). \tag{2}$$

where τ_{K} is relaxation time of a Kuhn step, $\mu_i \equiv (\partial F/\partial N_i)$ is chemical potential of strand i and ΔW_i is Wiener increment with zero mean and variance Δt. Entanglements are created or destructed only chain end by reptation. In monitoring N_i at end strand, when N_i becomes less than given minimum, an entanglement is destructed. On the contrary, N_i becomes more than

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given maximum, an entanglement with any surrounding strand within $a_0 = N_e b^2$ is created. N_e is the average number of N_i. The number window of N_i is given by

$$0.5N_e < N_i < 1.5N_e. \tag{3}$$

Dynamical equation of $\mathbf{R}_i$ is written as

$$\mathbf{R}_i(t+\Delta t) \cong \mathbf{R}_i(t) + \kappa \mathbf{R}_i(t)\Delta t - \frac{N_e b^2}{12 k_B T \xi \tau_e}\left[\left(\frac{\partial F^\alpha}{\partial \mathbf{R}_i}\right) + \left(\frac{\partial F^\beta}{\partial \mathbf{R}_i}\right)\right]\Delta t + \sqrt{\frac{N_e b^2}{6\xi\tau_e}}\Delta \mathbf{W}_i, \tag{4}$$

where $\tau_e = N_e^2 \tau_K$, ξ is time ratio of τ_e and constraint release time and α and β indicate test chain and another chain sharing the entanglement locating at $\mathbf{R}_i$.

It has been confirmed that distribution of N (Fig. 1) is consistent with the theoretical prediction [4]. Tests for other quantities and chain dynamics shall be discussed elsewhere.

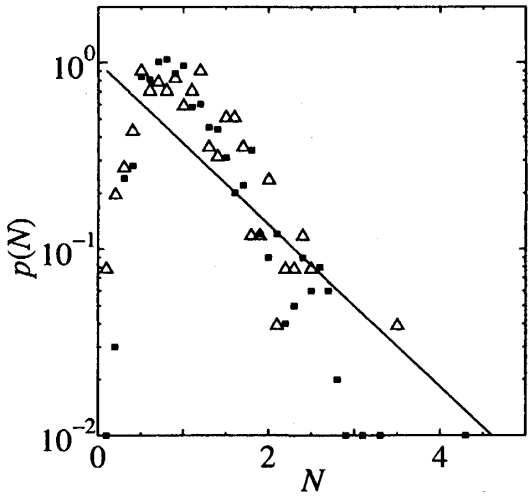

Figure 1: The simulated distribution (open triangle: ensemble average, closed square: time average) of number of Kuhn steps in a strand compared with the theoretical prediction(line) [4]

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